Supplemental Information

Solvent-tuned Hierarchical Porosity in Nitrocellulose Aerogels

Geneva R. Peterson[†], Katie A. Cychosz[‡], Matthias Thommes[‡], Louisa J. Hope-Weeks[†*]
[†]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock TX 79409
[‡]Quantachrome Instruments, 1900 Corporate Drive, Boynton Beach FL 33426

Materials

Nitrocellulose was obtained as Collodion solution (4-8% nitrocellulose in 50/50 diethyl ether/ethanol) from Aldrich (Catalog number 09986). Ethanol, 1-butanol, 2-propanol, methanol, hexanes, diethyl ether, acetonitrile, and ethyl acetate were obtained from Fisher and used as received. Octyltrichlorosilane was from Sigma Aldrich.

Preparative Methods

Nitrocellulose gels were prepared in three dram glass vials which had been silanized[1] with octyltrichlorosilane, otherwise the aerogel adhered tenaciously to the glass mold and could not be removed without substantial mechanical damage. Gels prepared in silanized vials were free to contract from the vial walls during supercritical extraction. The original gels are right cylinders of 15.5 mm height and 16.9 mm diameter (Volume = 3.5 cm^3). After critical point drying some syneresis had occurred leading to aerogels of ~1.4 cm height and 1.45 cm diameter (Volume = 2.3 cm^3), hence a 34% shrinkage. (See Figures S2(d) and S3). The aerogels weighed 110-115 mg each regardless of solvents used in the gel preparation. Hence the bulk density of the nitrocellulose is 0.05g/cm^3.

Silanation was achieved by filling the vials with hexanes, adding one drop of octyltrichlorosilane from a Pasteur pipette, capping the vial, shaking, and allowing to stand for at least two hours. Thereafter, the vials were emptied, rinsed with fresh hexanes, and dried under ambient conditions or with an air stream.

Nitrocellulose alcogels were prepared by adding 2 ml of Collodion solution to a silanized vial followed by 2 ml of a co-solvent. The vial was capped, vortexed, and the solution allowed to fully run down the walls of the vial again. Thereafter the gel was either (1) uncapped and left under ambient conditions until it had "set" to form a gel, or (2) hexanes was carefully layered over the Collodion solution by pipette and the vial was capped until the nitrocellulose had fully gelled (**Figure S1**).

SPIDRY critical point driers were used to dry the nitrocellulose gels. In the case of gels prepared by precipitation, the supernatant solvent was decanted prior to loading in the critical point drier Typically, five alcogels were processed over three days of solvent exchange with liquid carbon dioxide prior to bringing the chamber past the critical point (40°C, 1200 psi). Then the chamber was vented over 6-8 hours until ambient pressure was reached.

[1] Doescher, M. S.; Pietron, J. J.; Dening, B. M.; Long, J. W.; Rhodes, C. P.; Edmondson, C. A.; Rolison, D. R., Using an oxide nanoarchitecture to make or break a proton wire. *Anal. Chem.* **2005,** *77* (24), 7924-7932.

Gelation Results:

As demonstrated in Figures S1 and S2, the use of different co-solvents in the formation of the nitrocellulose gels produces very different results. These results can be understood in terms of a precipitation mechanism. A gel is a bicontinuous network of porous solid which entraps and immobilizes a relatively large quantity of fluid. Hence, in order for a gel to form, the nitrocellulose must precipitate from solution while yet sufficient solvent is present for the solid nitrocellulose to engulf and entrap it. This occurs with ethanol, 2-propanol, and 1-butanol which indicates that these solvents are effectively "borderline good" solvents for nitrocellulose – they support the dissolution of the polymer and mediate its gradual precipitation in the presence of a large bulk of solvent, thereby forming stable gels. This happens either by slight concentration of the polymer solution by evaporation, or at the interface of the nitrocellulose solution with a non-solvent such as hexanes.

On the other hand, acetone, ethyl acetate, acetonitrile, and methanol are too effective as solvents for nitrocellulose to enable the precipitation of a solid matrix of nitrocellulose while there is still a large volume of solvent present. Hence, when attempting to form gels by evaporation of methanol, acetone, ethyl acetate, or acetonitrile, the nitrocellulose solution becomes more and more concentrated, but does not precipitate. Rather, the loss of solvent results in a more and more concentrated solution of nitrocellulose until all solvent is lost and a solid film is formed (Figure S2b). Similarly, when hexanes is used as a non-solvent, these solvents still hold nitrocellulose in solution until the hexanes completely mixes, at which point the nitrocellulose is abruptly precipitated as a dense mass (Figure S2a).

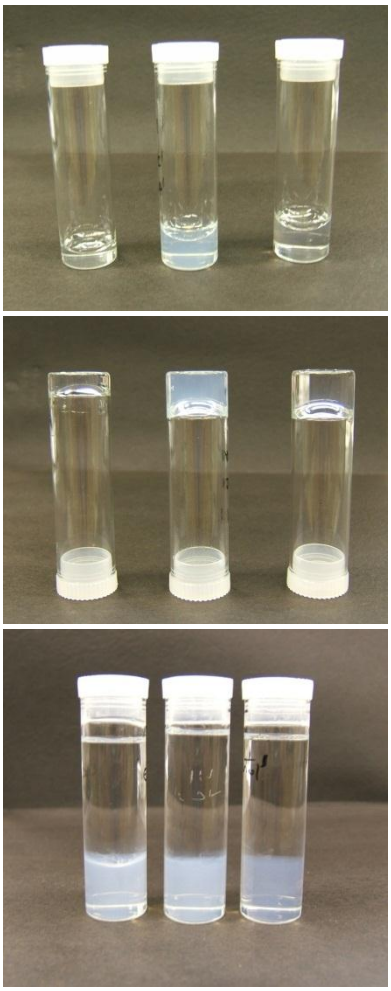
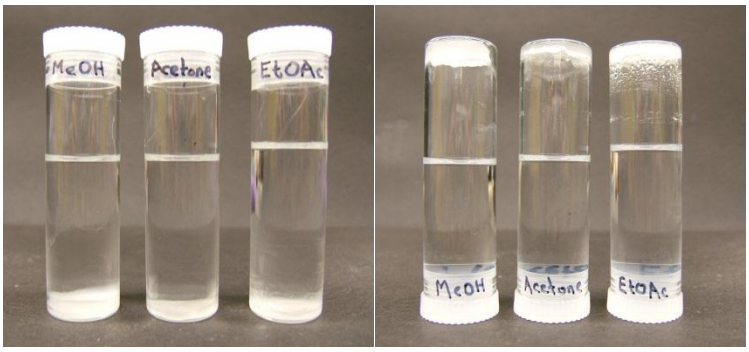
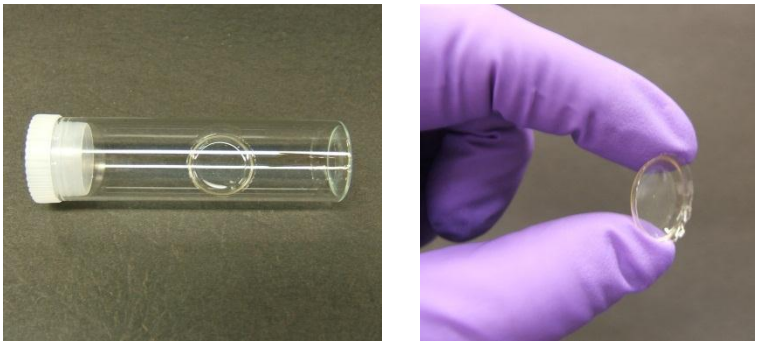


Figure S1: *Top and middle:* NC alcogels by evaporation; *Bottom:* NC alcogels by precipitation with hexanes. In each case, ethanol=left, 2-propanol=middle, butanol=right.

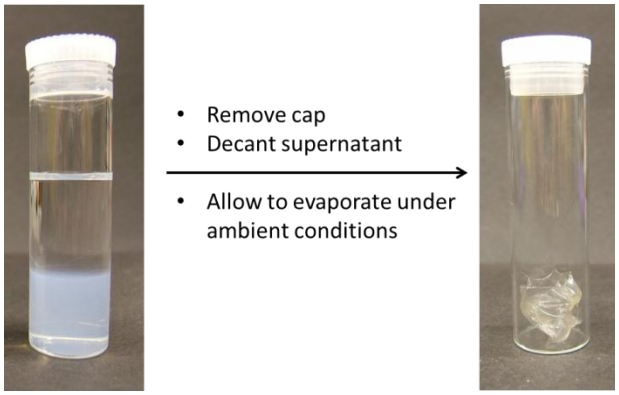
a.



b.



c.



d.

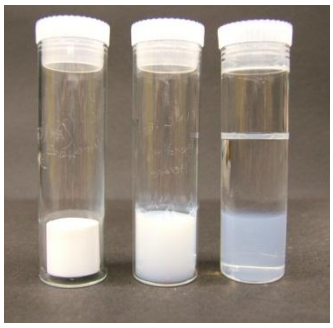


Figure S2: *a:* Methanol, acetone, and ethyl acetate do not serve as stabilizing co-solvents for the formation of nitrocellulose gels by precipitation with hexanes. *b*: Use of the above co-solvents also fails to produce an intermediate gel phase upon evaporation. Instead, the solution gradually reduces in volume until a film is formed at the base of the vial. *c:* Nitrocellulose alcogels are not stable to ambient drying; they collapse to form films, not xerogels. *d*: From left to right, nitrocellulose gel prepared in a silanated vial, having withdrawn from the glass; nitrocellulose gel prepared in a non-silanated vial adhered to the glass; alcogel.

Figure S3: *left:* Nitrocellulose alcogels with increasing quantities of diethyl ether in the co-solvent (0%, 25%, 50%, 75% and 100% by volume, left to right); and *right*: the corresponding aerogels after critical point drying with carbon dioxide.

Instrumental Methods

Physisorption Analysis

Nitrocellulose specimens were degassed prior to physisorption analysis at 50°C for 20 h. Specific surface areas were determined from nitrogen sorption data collected on a Quantachrome Nova 4200e pore size analyzer at 77K. Data were processed using NovaWin 11.0 software. Multipoint BET surface areas were calculated from five data points in the relative pressure range of 0.05-0.3 of the adsorption branch. Three surface area determinations were made from different specimens of the same sample type.

High resolution isotherms were collected for gels prepared in 100 % ethanol and 100 % diethyl ether co-solvents on a Quantachrome Autosorb iQ Pore Size Analyzer with equilibration times of 3 min. Isotherm data were processed using ASiQwin 2.0 software. In the case of the aerogel prepared in 100 % diethyl ether, pore size distribution was calculated using the QSDFT N_2 on carbon, cylindrical pore, adsorption branch model. A moving point average of 11 was chosen. For the aerogel prepared in 100 % ethanol, the pore size distribution was calculated using the BJH model; the carbon black t-method and a moving point average of 5 were utilized.

Scanning Electron Microscopy

Scanning electron micrographs were collected on a Hitachi S5000 scanning electron microscope with an accelerating voltage of 2kV. The nitrocellulose gels were torn and mounted on carbon tape with their interior surfaces facing upward. The mounted specimens were then sputter coated lightly with Pt/Au at 10 volts and 5 milliamps for 30 s. Some specimens required a second coating to sufficiently dissipate charge under imaging conditions.

The nitrocellulose gels proved highly sensitive to the electron beam. This sensitivity manifests itself by gradual shrinking/collapsing of the porous gel structure. This effect is accelerated by high magnifications and slow scan rates required for image acquisition. Hence, the SEM images obtained provide only relative and qualitative morphological information. An example of the sensitivity observed is given below (**Figure S4**) in which an area of a gel prepared in 50% Et_2O/BuOH was first imaged at 5k×, then at 10k×, and then once again at 5k×. These images show the progressive shrinking of the fine mesh domains of the hierarchical porous network with concomitant increase in the size of the large channel spaces. Similar sensitivity was observed in all specimens of NC gels.

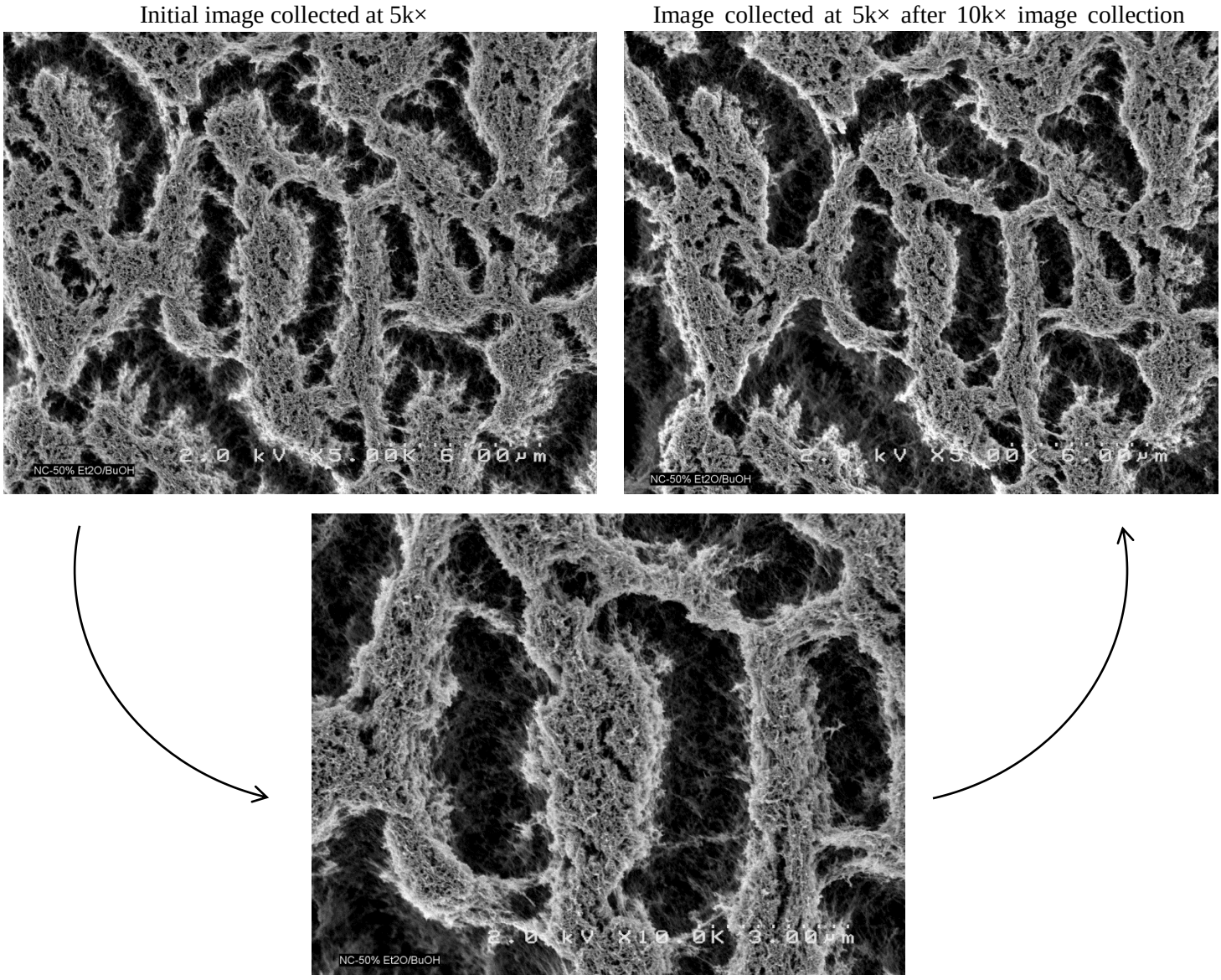
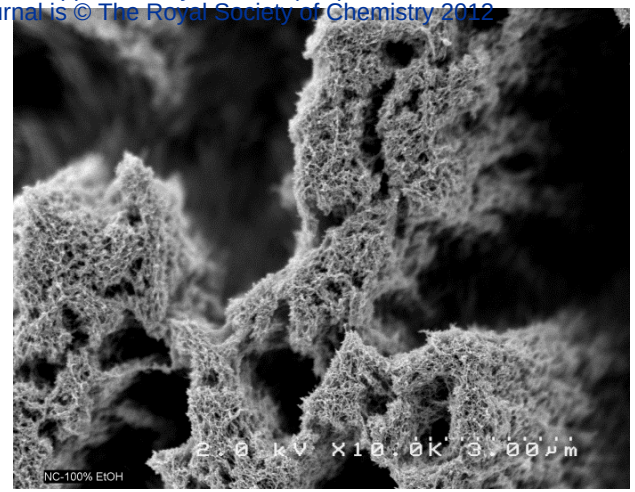
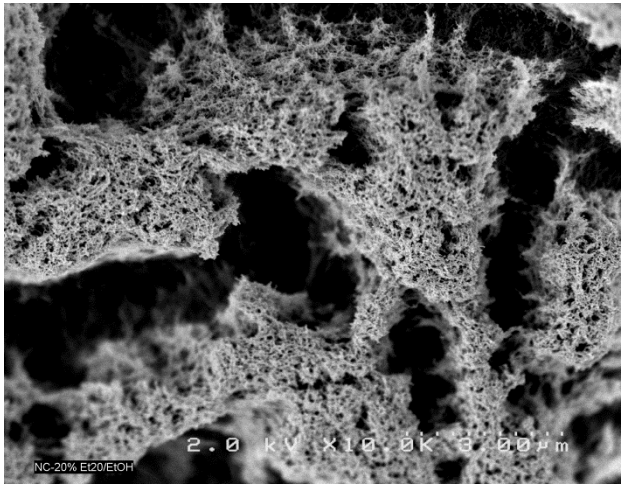


Figure S4: Example of NC aerogel response to the scanning electron beam at slow scan rates required for image acquisition and high magnifications; Note the change in the two 5k× images before and after image acquisition at 10k×

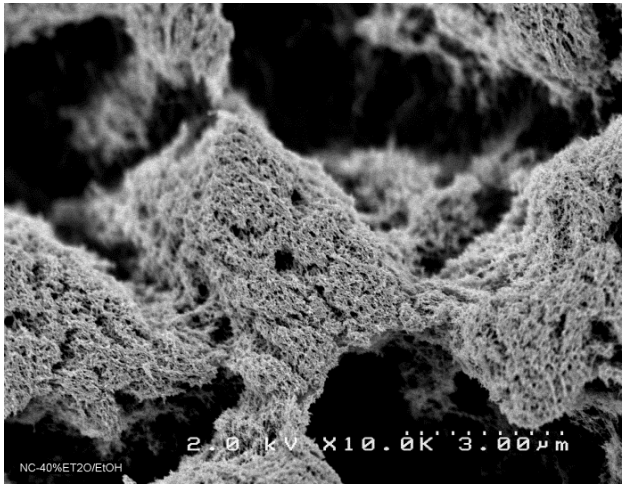


100% EtOH

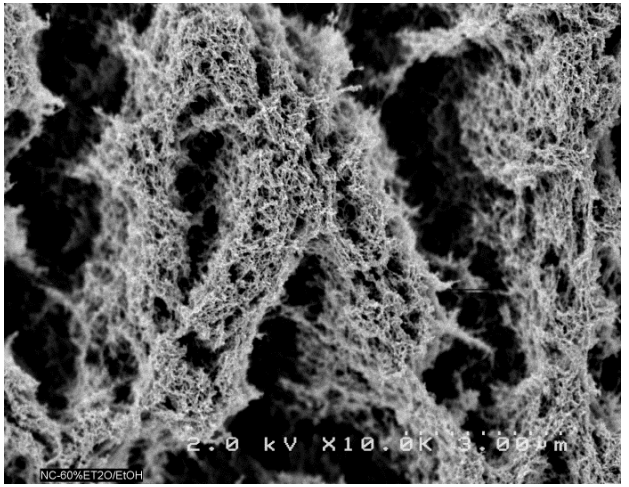
Figure S5: Scanning electron micrographs (10k×) of nitrocellulose aerogels prepared in varying mixtures of ethanol and diethyl ether (Et_2O). They are grouped here to facilitate comparisons while the full-sized high resolution images are shown on the following pages.



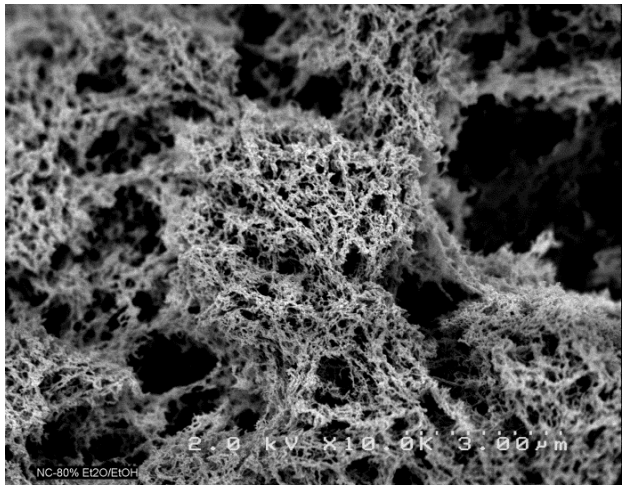
20% Et_2O



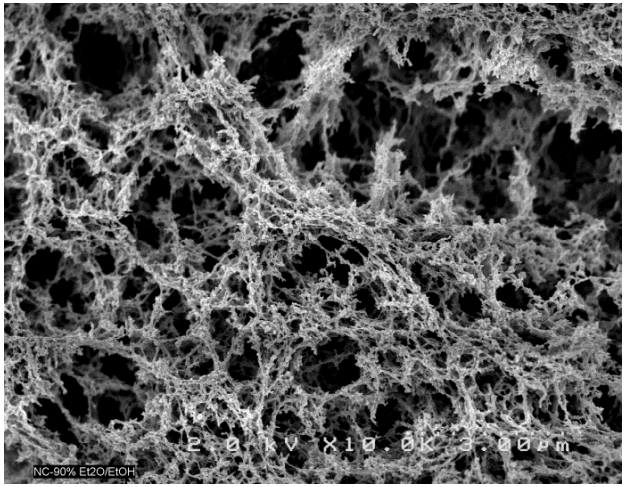
40% Et_2O



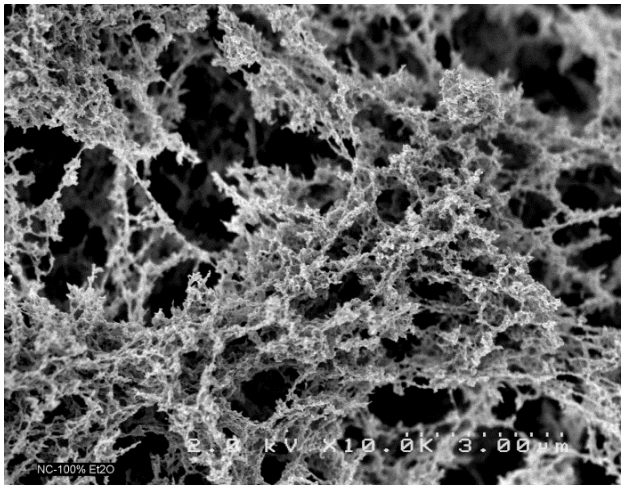
60% Et_2O



80% EtOH



90% Et_2O



100% Et_2O